

The Electric Discharge in Monatomic Gases

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92 Messrs. F. Soddy and T. D. Mackenzie. [Oct. 8,

ordinary silver of corresponding thickness and size. The films during this change of resistance altered neither in reflecting power nor in appearance when viewed by transmitted light.

As reflecting silver films of very different thickness and initial resistance and produced under very different conditions all showed this great increase in conductivity, Oberbeck concluded that when silver is first deposited from aqueous solution in the form of a mirror, it is in a different molecular condition from ordinary silver, but that in time its state approaches that of the latter more and more.

The Electric Discharge in Monatomic Gases.

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(Communicated by Professor J. Larmor, Sec. R.S. Received October 8,—
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1. Scope of the Enquiry.

In a recent paper* one of us has described the use of metallic calcium at high temperature for the production of high vacua, and in spectroscopic work as a very perfect chemical absorbent of all except the chemically inert gases. It was shown that helium and argon purified by calcium from traces of common gases or vapours, with which they are in practice invariably contaminated during manipulation, showed a great disinclination to conduct the discharge. In ordinary spectrum-tubes, helium offered a resistance equivalent to an alternative spark-gap of an inch in air, at a pressure of 0.05 mm., and argon at 0.02 mm. of mercury. This behaviour of the monatomic gases, together with the closely-allied phenomenon shown by spectrum-tubes filled with these gases of becoming non-conducting, or "running out," under the action of the discharge, have now been investigated in detail. A great number of experiments have been performed and a short summary will be given in the present paper.

The main object was to settle whether electric conduction in the monatomic gases is essentially different from that in other gases. The first results raised at least a presumption that perfectly pure helium might

* 'Roy. Soc. Proc.,' 1907, A, vol. 78, p. 429.

be unable to conduct the discharge at all, so that the running out of spectrum-tubes might be due to the absorption of the impurities only by the electrodes and not by the absorption of the inert gas itself. This view, however, proved to be untenable.

The absorption of the monatomic gases during the discharge occurs rapidly and continuously under suitable conditions, and the nature of this action is now fairly clear. But, on the other hand, helium which has been subjected to the prolonged action of the discharge between aluminium electrodes, after initial purification with calcium, exhibits to an altogether extraordinary degree the peculiarity before noticed. In an ordinary spectrum-tube such helium offers a resistance equivalent to that of an inch spark-gap at a pressure of over half a millimetre of mercury, and the discharge is accompanied by all the well-known characteristics—intense fluorescence of the tube, production of cathode rays, and the incipient production of X-rays—which are usually supposed to be indicative of a high vacuum. But at higher pressures this very pure helium conducts the discharge in the same way as other gases. Our results leave no doubt that the difference between helium and other gases is one of degree only, and that the monatomic gases are relatively electrically as well as chemically inert. It will be shown that the remarkable behaviour of helium in the region of low pressure is intimately bound up with the equally remarkable behaviour of the gas in the region of atmospheric pressure, when, as Ramsay and Collie* have shown, it conducts the discharge so much more easily than any other gas. A spectrum-tube filled with helium at atmospheric pressure conducts the current from a small induction coil with ease. It is only necessary to regard the helium molecule at all pressures as only about one-fifth to one-tenth as effective electrically as a molecule of a common gas like hydrogen, in order to obtain a simple and consistent explanation of the behaviour of both high and low pressure helium to the discharge. In the course of the work it became necessary to examine the common gases also in order to be able to compare their behaviour with the monatomic gases. The result transpired that the electrical effects usually supposed to be indicative of a high vacuum occur in all gases at degrees of rarefaction which cannot with any accuracy be described as “high vacua.” Thus in the previous paper the behaviour of argon, which was found unable to conduct below 0.02 mm., was regarded as exceptional. In reality, it is similar at this pressure to the common gases, hydrogen and nitrogen, all of which, when pure, cease to conduct at about 0.04 mm. The pressure in an X-ray tube, filled with hydrogen and giving good X-rays, is above

* ‘Roy. Soc. Proc.’ 1896, vol. 59, p. 257.

0.01 mm. Some of the possible causes which may have contributed to the mistaken impression that the degree of rarefaction in a Crookes tube is of the order of a thousandth of a millimetre will be discussed in the paper.

During the investigation it transpired that the spectrum of one of the rare gases appeared in a set of new spectrum-tubes during preliminary preparation before any of the gas had been introduced; and it has been put beyond doubt that the aluminium electrodes of spectrum-tubes which have been used with either helium, neon or argon, retain, even after months' exposure to the air, sufficient of the gas in question to give its spectrum when remounted in a new glass tube into which none of the gas is introduced.

2. *Absorption of Helium in Spectrum-tubes.*

In our first series of experiments the running out of spectrum-tubes filled with helium was investigated. Six similar spectrum-tubes of about 28 c.c. volume were filled with helium purified by calcium to accurately known initial pressures, ranging from 1 to 32 mm. The tubes were constructed to stand a heavy current without breaking down. The cathode consisted of aluminium wire 4 mm. diameter, and the anode an aluminium disc 16 mm. diameter. A narrow side tube was sealed into the cathode chamber for the purpose of measuring subsequently the residual gas in the tube, and a tube drawn to a fine point, to be broken under mercury at the end of the experiment, was sealed to the anode chamber. These tubes were constructed in batches of a dozen at a time by a well-known London maker especially for the investigation, and none of them have been used in any other experiments.

Six tubes at a time were attached to the calcium furnace, an arrangement for admitting known quantities of helium, and a mercury pump, and very thoroughly freed from occluded gases by heating and passing a discharge heavy enough to fuse the electrodes. The remarkable fact must be chronicled that during this treatment, before any helium had been brought into the apparatus, the first batch of tubes developed the helium spectrum. In the two first experiments, each with six new tubes of the first dozen, the full helium spectrum was developed during the preliminary treatment. The second batch of a dozen, made at another time, did not show this behaviour. The phenomenon and its probable explanation are discussed under Section 9.

The practice adopted during this preliminary treatment was to keep the calcium at its absorbing temperature, and by a tap to regulate the flow of expelled gases into the calcium chamber, so as to keep the tube fluorescent without allowing the vacuum to rise to the non-conducting point. When the operation was complete and the calcium had absorbed the expelled gases,

helium was introduced, the fusion of the electrodes repeated, and the tubes again exhausted by the pump. This was necessary, as it is known* that electrodes freed sufficiently from occluded gases by ordinary running and heating tend to evolve a further supply when filled with the monatomic gases and run, owing to the much greater heating of the electrodes in the latter gases.

Helium in accurately known amount was then admitted to the calcium chamber and allowed to remain there until the spectrum became perfectly pure, when the tap to the spectrum-tube was opened and the first tube sealed off. The remaining five were then sealed off one by one, each after a further known quantity of helium had been admitted. The total volume of the apparatus had been found, so the initial pressure of helium in each tube could be calculated.

The six tubes were then run in series with a heavy current from a 10-inch coil worked with a mercury interrupter from the 250-V. mains. A rectifier was placed in the secondary circuit to keep the current as unidirectional as possible, but it is doubtful if this had any influence. The first four tubes showed a sharp line spectrum, but in the other two, owing to too high pressure, the spectrum was confused. A new clear faint line in the extreme red, about 7266, was noticed in the helium spectrum of the tubes filled at lower pressure.

The first three tubes ran out and became non-conducting without difficulty, and ultimately the fourth also, but the remaining two did not. All the first four tubes went through the same changes in appearance just before they became non-conducting. The glow changed from yellow to green, and the yellow line, at first by far the strongest, became weaker than the green. At this stage the cathode fluorescence extended a distance of 12 cm. to the extreme tip of the side gauge-tube. As soon as the discharge commenced to pass an alternative gap of 1 inch in parallel to the tube, the latter was cut out of circuit and the tip broken under previously heated mercury, with precautions against the admission of air. As the mercury entered, all the gas was compressed into the side gauge-tube and its volume marked by a diamond scratch. The table (p. 96) shows the details of the six tubes.

The current after the first 40 hours was considerably increased.

The pressures in the last column were obtained from the volume of the residual gas immediately after filling the tube with mercury. It will be seen that the helium is absorbed during the discharge until a residual pressure is reached nearly the same in each case and between 0.6 and 0.7 mm., independent of the initial pressure. This indicates that at this pressure the

* E. C. C. Baly, 'Phil. Trans.,' 1903, A, vol. 202, p. 185.

	Initial pressure.	Fluorescence appeared.	Became non-conducting.	Residual pressure.
	mm.			mm.
I	1·1	From start	After 25 mins.	0·57
II	2·3	After 10 mins.	After 70 mins.	0·72
III	4·9	After 50 mins.	After 7 hrs. 40 mins.	0·62
IV	8·6	After 60 hrs. 30 mins.	After 61 hrs. 20 mins.	0·9
V	16·8	} Did not appreciably change after over 100 hours' continuous running.		
VI	31·2			

helium ceases to conduct the discharge. But it was at once found that as soon as the mercury entered the tube it commenced to dissolve the mirror of aluminium deposited from the electrodes and to liberate the absorbed gas. In the first tube, after the volume of the residual gas had been measured, the mercury was sucked out and allowed to refill the tube, when the volume was found to have doubled. In the second tube the evolution of gas could be watched, and large bubbles made their appearance at the cathode film as the mercury was sucked out. The volume after refilling corresponded to a final pressure of 1·33 mm. In the third tube, after the mercury had been left in half an hour, the pressure was 3·43 mm., and after readmitting the mercury and allowing it to remain another four hours the pressure was 3·7 mm. In the fourth tube gas came out from both the anode and cathode mirrors, and the volume increased enormously, but the final measurement was unfortunately lost. The spectrum of the residual and liberated gas was always observed, to detect the entrance of air, but in every case the spectrum, except for mercury, was of absolutely pure helium.

These experiments clearly show the nature of the process when a helium tube is run to non-conductance. Contrary to what was given as the explanation in the last paper,* a real absorption of the helium takes place, and the greater part of the absorbed gas is very loosely retained and can be recovered from the aluminium mirror volatilised from the electrodes. On the other hand, non-conductance obtains in pure helium long before all the helium is absorbed, and the gas so treated refuses to conduct the current at a pressure when any other gas would be at about its maximum conductivity. As, however, the residual pressure was practically the same for all the four tubes, one of which had been run for over 60 hours, the experiments do not support the idea that pure helium by itself is a non-conductor. They favour the view that the constant residual pressure is the real limiting pressure for pure helium itself, above which it will conduct in the same way as any other gas.

* *Loc. cit.*, p. 448.

The experiments described are inconclusive in one respect. Owing to the unexpected ease with which the absorbed gas is liberated under the action of mercury, the large residual pressures observed might have been due at least in part to liberation of absorbed gas during the admission of the mercury. This did actually happen in the filling of Tube No. IV with mercury, and accounts for the somewhat high residual pressure observed. Before the cathode chamber had filled actual bubbles had been liberated from the aluminium film in the anode chamber and could be seen passing through the capillary with the entering mercury. It was, therefore, necessary to repeat the observations in a different manner to eliminate this uncertainty.

Before describing these it may be mentioned that a similar series of tubes to those used for helium were prepared with argon, but none of the tubes could be run out to non-conductance even after prolonged action of the discharge. During the greater part of the time the cathode in the tube filled at lowest pressure (1.3 mm.) was bright red-hot. Only this tube showed a clear spectrum. All the others filled to higher pressures had a confused spectrum. In filling the tubes we had the mistaken impression that argon was more easy to run out than helium. Argon spectrum-tubes certainly often run out more readily than those of helium, but this is due to the fact that the pressure in an argon tube is necessarily so much lower than in helium in order to get a clear spectrum. A good helium tube may be filled to 6 or 8 mm. without confusing the lines, but in argon the pressure should not be much over a millimetre. To get results with argon comparable with those for helium the tubes should have been filled to about one-tenth the pressures.

3. *The Pressure at which Pure Helium ceases to conduct.*

The advantage of experimenting with sealed tubes is that thereby the influence of contaminations derived from lubricants and mercury is eliminated. In the present series of experiments mercury vapour was present, and found not to exert any important influence; but lubricants were completely avoided in that part of the apparatus containing the helium while it was being run. The spectrum-tube was of the same pattern as before, but was kept connected throughout the experiment with a specially designed form of McLeod gauge (fig. 1) by means of an unstricted tube. The graduated tube and the connecting tubes were 6 mm. in bore, and to avoid the latter being too long they were provided with glass valves closed by the rising mercury of the kind usually found on Töpler pumps. The gauge was worked without rubber tubing by varying the pressure on the mercury in the reservoir. By the special arrangement of tubes shown, the

spectrum-tube and gauge could be connected with or shut off from the rest of the apparatus by lowering or raising the mercury, so that the apparatus constituted a mercury tap as well as a gauge. Thus the vapour of lubricants was avoided, and during the running of the spectrum-tube the mercury sealed off the connection with the rest of the apparatus. With this

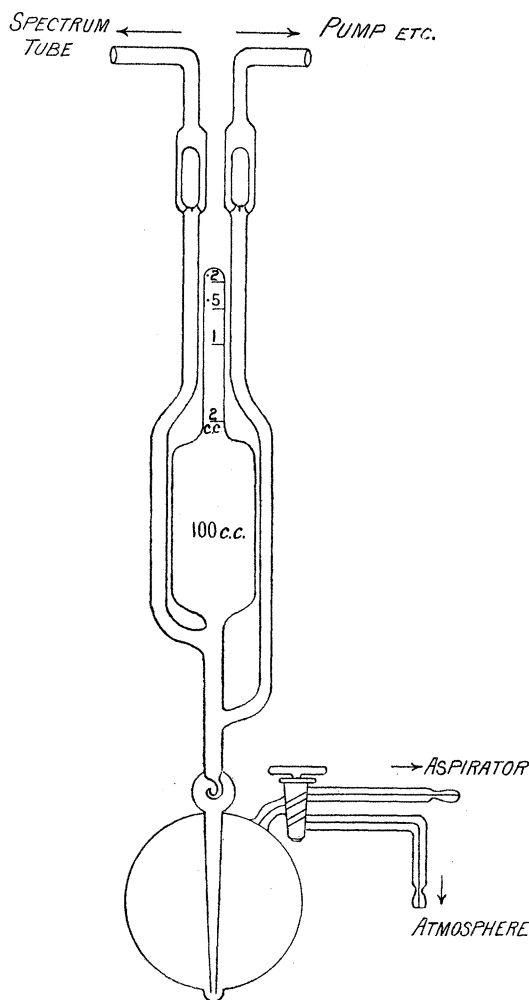


FIG. 1.

apparatus the earlier results were at once confirmed. If helium purified by calcium is admitted in successive small doses to the apparatus and run out till the discharge commences to pass an inch gap, the pressure at which non-conductance obtains reaches a maximum of 0.7 mm., and then the admission of more helium and further running to non-conductance always

reproduces this same pressure. In common gases the stage of non-conductance is usually reached very abruptly at a definite pressure, but in the monatomic gases a heavy current will partly spark across a given gap when a feeble current would pass entirely through the tube. The observations were, therefore, taken under as nearly comparable conditions as possible as regards the current flowing. Three stages were recognised in the experiments. In the first, sparks passed regularly at intervals of a few seconds; in the second, sparking was continuous, about half the current going through the gap; and in the third, only a very feeble current passed through the tube. The initial passage of a single spark or a few sparks at long irregular intervals across the gap was ignored. The pressure of 0.7 mm. corresponds to the first stage. If the pressure is measured after the second stage is reached, it is found to be about 0.55 mm. When the discharge is left to run for several hours until the third stage is reached and hardly any current passes through the tube, the pressure sinks to 0.35 mm., and does not further decrease however long the discharge is continued. Increasing the spark-gap to 2 inches only effects a very slight additional absorption of the gas, and external discharges take place over the glass, owing to the condenser effect of the aluminium mirror inside the tube, which involve the risk of puncturing the tube.

In this apparatus the pressure at which sparks from a small coil commenced to jump an inch gap was measured in helium which had been purified by calcium only and not subjected to the discharge. It was found to be 0.275 mm. This is over five times the pressure given in the last paper, and is due to a more thorough removal of gases from the electrodes prior to the experiment, and to the absence of vapour of lubricating grease. It is clear that running the tube exerts a further purification of the helium by the absorption of the last remaining impurities in the electrodes, and that an otherwise undetectable trace of impurity makes a very great difference on the pressure at which helium becomes non-conducting.

In helium purified by calcium and the prolonged action of the discharge, examined in a straight tube 30 mm. wide by 100 mm. long, with two 10 mm. discs of aluminium 42 mm. apart, continuous sparking across an inch gap occurred at a pressure of 0.39 mm. The total amount of gas admitted to this tube during the experiment was recorded. The tube was pumped out to 0.001 mm. On standing for 20 minutes the pressure had risen to 0.01, and after 18 hours to 0.034, due to the spontaneous liberation of helium in the cold. The tube was then heated, and the pressure rose to 0.36 mm. It was pumped out to 0.001, and reheated more strongly, when the pressure of the gas liberated was 0.5 mm. It was

calculated that at least 98 per cent. of the absorbed gas was re-evolved through heating. As at this temperature none of the gas which causes the Campbell Swinton effect (compare Section 10) is liberated, it follows that only a very small fraction of the absorbed gas is driven into the glass itself.

Experiments were made to see if helium is absorbed during simple volatilisation of aluminium and magnesium by heating these metals in a furnace similar to that employed for heating calcium. No absorption occurred. This suggests that the absorption in the case of helium is electrical or mechanical rather than chemical. The gas molecules moving under the electric force with great velocity resemble the α -particles, and are able, as Campbell Swinton's results indicate, to penetrate the surface of the glass wall to a very slight extent and remain embedded. If, however, the glass is covered with a mirror of aluminium, most of the gas is stopped there and does not reach the glass.

An arrangement was devised to compress helium after it had been purified by calcium and run till non-conducting in a spectrum-tube without thereby contaminating it. A second volume of about 100 c.c., capable of being filled with or emptied of mercury in the same way as the M'Leod gauge, was attached to the apparatus. The whole apparatus was first filled with helium and run to non-conductance, and mercury was then admitted to compress the helium, and the spark-gap measured. It was found that the gas behaved quite normally. Increasing the pressure lowered the spark-gap, and on expanding the original spark-gap was regained. The helium, owing to the larger volume of the apparatus, was not quite so pure as before, and the pressure in one experiment with the sparks passing an inch gap was 0.43 mm. At 0.68 mm. the gap was 12 mm., and at 1.64 mm. the gap was 3 mm. An attempt was made to get an approximate value in volts for the various spark-gaps by means of current from a large Wimshurst machine and a Kelvin electrostatic voltmeter. The gap of an inch or 25 mm. corresponded to 16,800 V., of 20 mm. to 12,500, of 10 mm. to 10,400, of 5 mm. to 7900, and of 2 mm. to 5100.

4. *Behaviour of Neon and Argon.*

The results obtained with neon and argon were quite analogous to those recorded for helium. With neon the first stage of non-conductance with an inch gap occurred at a pressure of 0.18 mm., the second at 0.10 mm. and the last at 0.07 mm. With argon a great many observations were made and the three pressures were 0.055 mm., 0.05 mm., and 0.04 mm. In one experiment with the latter gas the initial pressure in the tube was 0.27, and

it took four hours' running before the tube became non-conducting. During this time the pressure steadily decreased until the values given above were reached. Increasing the gap to 2 inches only effected a slight reduction of pressure to 0.037 mm. In an experiment with neon which had been run to the last stage and left, the pressure rose during the night from 0.075 to 0.09, and on heating the tube next morning a pressure of 0.4 mm. developed. Only 30 seconds' running sufficed to reduce this to 0.2 mm., when sparks commenced to jump the gap.

5. *Behaviour of Hydrogen, Nitrogen, and Carbon Dioxide.*

Similar experiments on the pressure at which non-conductance obtained were performed with the gases hydrogen, nitrogen, and carbon dioxide. With these the non-conducting point was very well defined. Thus with hydrogen practically no current went through the tube at a pressure of 0.04 mm. for a spectrum-tube, and 0.03 mm. for a wide tube of the kind described (p. 99). It was found that pure hydrogen, derived from palladium hydride, behaved in the same way as the gas introduced into the apparatus by heating, with a spirit flame, the palladium wire of a regulator such as X-ray bulbs are now commonly provided with for lowering the vacuum. Cathode fluorescence commences in hydrogen in a spectrum-tube at 0.1 mm., the gap was 5 mm. at 0.07 mm., and 10 mm. at 0.06 mm. In nitrogen non-conductance is reached at about 0.035 mm., and in carbon dioxide at about 0.02 mm., both for an inch gap. At a pressure at which a hydrogen tube would give an inch gap a carbon dioxide tube would give only a millimetre gap.

[Special experiments were performed with pure nitrogen to ascertain whether, after prolonged running, the pressure at which non-conductance set in was raised as in the case of helium, but with negative result. In a tube in which repeated additions of nitrogen were absorbed by the electrodes under the discharge, the pressure at which non-conductance occurred with an inch gap was the same at the end of the experiment as at the beginning with nitrogen which had not been run.—October 21.]

The gas generated from the electrodes and walls of a new spectrum-tube during running behaved, as its spectrum indicates, like a mixture of hydrogen and carbon dioxide and with an inch gap is non-conducting at 0.03 mm. It is remarkable how abruptly conducting power ceases when the pressure falls lower than 0.04 to 0.02 in common gases. The application of powerful coils may cause a discharge below these pressures, but only by first lowering the vacuum. The facilitation of the discharge by the use of electrodes of the alkali metals or calcium is analogous.

The action of these metals is probably to supply hydrogen sufficient to conduct the discharge. The evolution of hydrogen from calcium during heating formed the subject of frequent reference in the last paper. In operating the calcium furnace enough hydrogen is always evolved on heating a fresh piece of calcium to make the vacuum a far better conductor of heat than air at atmospheric pressure. Probably hydrogen-free calcium has never yet been prepared.

There are probably many other reasons, more or less well recognised, that account for the impression that the degree of rarefaction in a vacuum incapable of conducting the discharge is extreme. Apparatus to be exhausted is usually made with a constricted orifice where it is to be sealed off. The free path of the gas becomes comparable with the diameter of this constriction at about 0.1 mm., or higher in heavy gases and vapours. Below this pressure there is properly speaking but slight difference of pressure between the two sides of the orifice, using the word *pressure* in a hydrostatic sense, even though on one side a perfect vacuum is maintained. Diffusion alone, not flow, operates to equalise the concentration of the gas on the two sides, and therefore gauge readings of pressure in apparatus connected to the gauge with a narrow orifice are not strictly pressure readings at all. A more important error, probably, of the readings is the usually invariable presence of vapour which a compression gauge will not detect and a pump will not remove. In the present measurements constrictions were avoided and vapours removed by the action of calcium, and these two facts probably account for the pressures at which non-conductance obtains being comparatively high. It is doubtful whether the lower pressure recorded in the case of carbon dioxide is real or due to the property of carbon dioxide of condensing on glass surfaces, vitiating the gauge readings.

6. *Behaviour of Mercury Vapour.*

In the first series of experiments the mercury was contained in an H-tube provided with two electrodes, and was connected to a shortened fall-tube, which, when the mercury was boiled out, acted as a Sprengel pump worked with the condensed mercury. After the apparatus had been exhausted as completely as possible by the mercury pump, the mercury in the tube was rapidly boiled and the exhaustion continued by means of the condensed globules of mercury falling through the fall-tube. Owing to the liability of the glass to crack during prolonged heating the method was abandoned. But with this apparatus the cathode fluorescence of the discharge was not observed when the temperature of the mercury was above 90°, and the tube was non-conducting to an inch gap below 60°.

1907.] *The Electric Discharge in Monatomic Gases.* 103

In the next experiments the apparatus was exhausted by means of calcium, the mercury being boiled vigorously, and a heavy discharge being passed through the tube during the operation. After this treatment the mercury remained non-conducting, and fluorescence was observed at much higher temperatures than if the calcium treatment had not been adopted. The cathode fluorescence was observed up to temperatures of about 110° , which corresponds to a pressure of 0.5 mm. The spark-gap was 10 mm. at a temperature corresponding to a pressure of about 0.15 mm., while below 0.1 mm. the mercury vapour conducted with difficulty. Hence mercury vapour resembles the monatomic gases both in the effect of impurities and the high pressure at which it remains non-conducting.

7. *Pressure in an X-ray Tube filled with Helium or Hydrogen.*

In order still further to test the view that helium conducts the discharge normally except for the higher pressure at which the various phenomena of the discharge make their appearance, an X-ray bulb of 8 cm. diameter was attached to the gauge in addition to the spectrum-tube, and the whole apparatus thoroughly freed from gas. Helium was admitted and run in the spectrum-tube till the discharge passed an inch gap at a pressure of 0.41 mm. The mercury in the gauge was then momentarily lowered, and small successive quantities of the helium removed by the pump, and the appearance of the X-ray tube observed. The hemispherical area of fluorescence accompanied by the production of X-rays just able to penetrate the glass was observed at a pressure of 0.31. At 0.25 mm. rays capable of penetrating 0.2 mm. of aluminium escaped the tube and the spark-gap was 1.5 mm. At 0.21 the spark-gap was 17 mm. and the bones of the hand could be well seen. At 0.15 mm. the spark-gap was 22 mm. and the flesh of the hand was quite transparent to the rays.

It must be pointed out in this experiment that the helium, though pure at the start, must have become contaminated as the pressure was reduced, owing to vapour from the rest of the apparatus diffusing back during the exhaustion, and to gas generated from the electrodes. For this reason the pressures corresponding to the longer spark-gaps are probably too low, and as the exhaustion proceeded, approached more and more closely to the values for a common gas like hydrogen. But, throughout, the appearance of the tube, but for the greenish glow at the commencement, was quite normal.

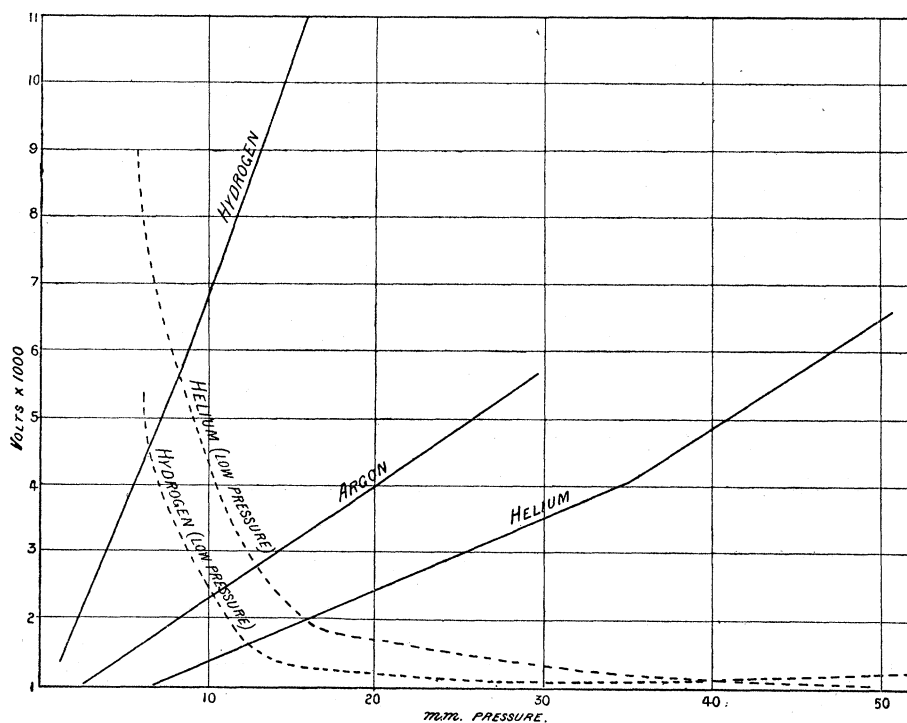
In the same X-ray tube, hydrogen derived from a palladium regulator gave the following values:—Fluorescence was plain at 0.13 mm., the gap was 10 mm. at 0.1, 20 mm. at 0.08, 30 mm. at 0.05, 40 mm. at 0.035, and 115 mm. at 0.02.

An X-ray bulb of the usual simple "bianodal" form and size, 13 cm. diameter, was attached to the gauge and exhausted entirely with the mercury pump in the ordinary way, the tube being heated in an oven and the discharge kept passing after the fluorescent stage had been attained. This operation took all day, whereas with calcium it could have been done easily within the hour. After cooling, the tube was run, and the pressures corresponding to different spark-gaps measured. The pressure varied from 0.008 mm. to 0.005 mm. with a gap from 4 cm. to 9 cm. The tube was then pumped as empty as possible, and subjected to the action of calcium to remove vapours. Hydrogen was then introduced through a palladium regulator. Now it was found that the pressures for corresponding spark-gaps were higher, and ranged from 0.045 with a spark-gap of 2 cm. to 0.012 with a spark-gap of 9 cm. It is probable that this difference is due to the absence of condensable vapours in the second case, and that in no case the real pressure in an X-ray tube is below the hundredth of a millimetre.

8. *The Relation of Potential to Pressure at High Pressures.*

On the view put forward to explain the high pressure at which helium becomes non-conducting, a space filled with a certain number of helium molecules conducts the discharge similarly in every way to the same space filled with about one-tenth to one-fifth the number of molecules of a common gas like hydrogen. This point of view at once brings into line the behaviour of helium at atmospheric pressure. At this pressure helium conducts the discharge in a similar manner to hydrogen at a pressure of several centimetres—that is to say, the discharge passes through helium at atmospheric pressure as a ribbon or flickering line of light. In order to investigate this point more closely, the curves connecting pressure and voltage in hydrogen and helium were compared in a very long wide tube by the aid of an 8-plate Wimshurst machine and a Kelvin electrostatic voltmeter. The current was kept constant, by regulating the speed of the machine, at about 0.3 milliampère. The voltage in hydrogen remained at a minimum of about 1100 V. from 0.62 to 0.3 mm., rising rapidly above and very suddenly below these limits. In helium the minimum potential was below 1000 V., the minimum range of the instrument, at from 6 to 0.54 mm. The tube was 70 cm. long, 25 mm. diameter, with two aluminium discs 15 mm. diameter, 64 cm. apart. The helium employed was spectroscopically quite pure at the commencement of the experiment, having been fractionated by charcoal cooled in liquid air, but no special effort was made to remove the unavoidable contaminations from taps, elec-

trodes, etc., introduced during the experiment. At 60 mm. the potential in helium was 7750 V., and in hydrogen this same potential was reached at 12 mm. In hydrogen at 30 mm. the potential was about 16,000 V., while in helium at the same pressure the potential was 3400 V. The smoothed curves are shown in the figure.



In the curves drawn in dotted lines the scale of the pressure axis is increased 100 times, so that these curves represent the relation of voltage with pressure up to 0.5 mm. In specially purified helium the curve would, of course, be very considerably displaced to the right.

The curve for argon at high pressure is also included in the figure, and it will be seen to approach helium more nearly than hydrogen. The fact that argon becomes non-conducting with an inch spark-gap at the same pressure as hydrogen does not truly represent the relation between the two gases, for at higher pressures up to the pressure of maximum conductivity, argon, like helium, conducts less readily than hydrogen, while in the region of high pressure it, like helium, conducts far more easily. The monatomic gases in general appear to be what has been termed electrically inert, and if the effectiveness of a molecule in allowing or resisting the passage of a discharge

is to be associated with the number of relatively free electrons it contains, the monatomic gases appear from their electrical, as well as from their chemical, inertness to be relatively deficient in easily displaceable electrons. But this point of view carries with it the corollary, since even in the purest state the monatomic gases are undoubtedly capable of conducting and becoming ionised, that their chemical inertness is relative rather than absolute. This was the view taken, we believe, by Dr. Larmor in connection with the previous paper.

Possibly the results described may be connected with the observations of Strutt,* who found the spark potential in helium and nitrogen greatly affected by minute traces of impurity, and of Warburg,† who found the cathode-fall in gases greatly affected by moisture and other impurities. But even if impurities exert a specific "catalytic" effect on the electrical properties of the gas with which they are mixed, apart from the effect proper to their partial pressure, it does not affect the conclusion that the monatomic gases are relatively electrically inert.

We wish to express our indebtedness to the Carnegie Trust for some of the apparatus used in the measurements given in this section.

9. *Retention of the Rare Gases by Aluminium Electrodes.*

In Section 2 it was recorded that a batch of new spectrum-tubes developed the helium spectrum during preparation, and the matter appeared to call for fuller examination. The conditions under which the spectrum-tubes were prepared were novel, in that the occluded gas was not pumped out, but absorbed chemically within the apparatus. Since six tubes with exceptionally heavy electrodes were treated at once, the conditions were very favourable for the detection of a minute trace of an inert gas produced by the discharge or evolved from the electrodes which otherwise would have been certainly overlooked. At first it was thought that the results might be connected with those of v. Hirsch,‡ who observed the continuous formation of a gas during the cathode-ray discharge, independently of the nature of the gas initially present, with properties which pointed to a possible molecular weight of 4. But Dr. von Hirsch about this time came and re-examined his gas in this laboratory by means of the calcium apparatus, and found it was certainly not helium.

A quantity of new aluminium wire and discs of the same kind as employed in the spectrum-tubes was procured from the maker of the tubes. This was heated to a very high temperature in a furnace similar to those employed for

* 'Phil. Trans.,' 1900, A, vol. 193, p. 377.

† 'Wied. Ann.,' 1890, vol. 40, p. 1.

‡ 'Phys. Zeit.,' 1907, vol. 8, p. 461.

calcium, but it failed to give the least indication of helium. Other spectrum-tubes at a later date from the same maker also did not give the least trace of helium when examined under conditions identical to those described.

The most probable explanation appeared to be that some of the electrodes in the first batch of tubes, probably the disc anodes, for the cathodes were almost certainly new, must have been old and used in previous experiments with helium before they came into our hands, and that such electrodes must be capable of retaining sufficient gas to show a spectrum when remounted in new tubes.

At the close of the investigation the second point was specifically examined. The electrodes of the tubes used in the experiments of Sections 3 and 4 were chosen for the test. The neon tube was first tried. It had been cut down five months before and since left open to the air. The cathode was first mounted in a new spectrum-tube with a new similar electrode fresh cut from a length of new aluminium wire of the same size and quality. It was attached to a calcium furnace through a tap and during the running the flow of gas was regulated to keep the tube fluorescent. As the spectrum cleared the neon yellow D_5 (5852.6) showed clear and distinct in the sodium, hydrogen, and mercury spectrum, its position being exactly fixed with reference to the two sodium lines. The tube was cut down and the disc anode of the old tube inserted in place of the new electrode, and then the tube was re-examined as before. Again D_5 was seen, but much brighter than before. After the calcium furnace had cooled, it was filled with mercury and the contained gas compressed about 15 times into a second spectrum-tube. Now the latter showed unmistakably to the eye the characteristic orange glow of neon, and the spectrum showed all the chief red and orange lines together with the helium line D_3 faint, and the lines of hydrogen and mercury. The original neon, which had been prepared by Mr. Berry by Dewar's fractionation method, showed the helium D_3 in about the same relative intensity. It can only probably be removed from the spectrum by fractionating the gas with liquid hydrogen. Contrary to the statement in Travers' "Experimental Study of Gases" (p. 312), the neon green line (5016) was not visible.

The helium tube was then examined. It had been cut down five months previously, but in this case had been sealed up, unexhausted, to exclude moisture. Both electrodes were sealed in a new spectrum-tube. The helium yellow D_3 was observed almost immediately after the commencement of running, and later the helium red (6677) faintly. From previous experience, the quantity of helium present could be accurately estimated. Its partial pressure was about 0.01 mm., and as the volume of the apparatus was about 200 c.c., the total quantity was about 3 cubic millimetres, measured at atmospheric pressure

This quantity would have given the whole spectrum brilliantly if the apparatus had been filled with mercury, but the result was certain without this being done.

The argon tube, like the neon tube, had been left open to the air for five months. The anode only was sealed into a new tube with a new electrode. It gave, on running, clear but faint argon lines in the blue region of the spectrum, and on compressing the gas at the end of the experiment the blue argon spectrum was clear.

[About a year previously, before any neon had been used in the laboratory, a number of old spectrum-tubes had been broken up and the electrodes recovered. These had since remained in an open dish exposed to air. A dozen of these electrodes, selected at random, were heated in a vacuum furnace to the melting point of aluminium, and the gases evolved absorbed by calcium in a second vacuum furnace. The helium yellow line, D_3 , was seen clear but faint. On compressing the gas about 14 times by admitting mercury, the prominent red and green lines of the spectrum were also seen. The quantity of helium was estimated to be about a fifth of a cubic millimetre.—*October 21.*]

These experiments, therefore, prove that aluminium electrodes tenaciously retain traces of argon, neon, and helium after they have been used in connection with these gases, and indicate that the explanation advanced for the extraordinary appearance of helium in the first batch of spectrum-tubes is probably correct and sufficient.

10. *The Campbell Swinton Effect.*

The glass parts of the spectrum-tubes, of which the electrodes had been used in the experiments described in last section, were examined for the effect described by Campbell Swinton,* who showed that if the glass of a vacuum-tube used with hydrogen or helium is fused in a flame it becomes clouded and under the microscope is seen to be permeated to some depth from the inside surface with a multitude of minute spherical bubbles. All three of our tubes showed this effect with the most remarkable clearness, but the argon tube was by far the best. Indeed, when the glass of this tube was fused it appeared to boil, and the bubbles could be seen and heard bursting. If the heating was stopped sooner the glass surface at first sight appears completely devitrified, but under a very small magnifying power the effect could be seen to be due to bubbles which were quite large where the glass had been most strongly heated. In the helium and neon tubes, and also the argon tube, the cathode chamber showed this effect everywhere where particles travelling at right angles to the surface of the wire cathode could reach the glass, but no effect whatever appeared behind the

* 'Roy. Soc. Proc.,' 1907, A, vol. 79, p. 134.

1907.]

The Electric Discharge in Monatomic Gases.

109

plane cutting the wire cathode at right angles drawn through the end of the glass tube in which the cathode was sheathed. The anode chamber of the helium and neon tubes showed a well-marked line of bubbles corresponding to the edge only of the anode disc, absent on the side where the side tube had been attached. In the argon tube this was absent, but the small part of the anode chamber immediately bordering on the capillary was strongly affected.

[The fact that the argon tubes showed the effect so prominently raised a doubt whether Campbell Swinton's explanation, that the bubbles are caused by the discharge gases being driven into the glass and remaining embedded below the surface, could be correct. Some of the glass from the argon tube was heated in an iron tube in a vacuum furnace, and the gases absorbed in a second furnace by calcium. The temperature, subsequently determined by a platinum and platinum-iridium couple, was in the neighbourhood of 1300°C . The glass frothed copiously, and was largely blown out of the iron tube. Argon, if present at all, could only have been but the merest trace as, although a faint argon spectrum was observed, it was not more than could be accounted for by a slight leak in the apparatus which interfered with the test. Certainly the main frothing of the glass was not due to embedded argon, and probably no argon was given off by the glass.

It was considered more satisfactory to try the glass of the neon and helium tubes in a similar way, as the appearance of these gases, if observed, is less equivocal than in the case of argon. No trace of neon was obtained from the glass of the neon tube which showed the Campbell Swinton effect strongly. With the glass of the helium tube the line D_3 was faintly visible. Some more of the glass was, therefore, first heated in an exhausted tube of Jena glass to a red heat to drive off gases condensed on the surface. The temperature was not high enough to develop bubbles, and the glass remained quite clear. This glass was then heated in a vacuum furnace as before to about 1300°C . No trace of helium was observed, even when the apparatus was filled with mercury.

These experiments show that the gas which causes the bubbles is not the discharge gas driven into the glass. The bubbles are in all probability a secondary effect, due to the chemical decomposition of the glass under the influence of local heating produced during the bombardment. There are probably in glass always sufficient undecomposed carbonates or sulphates to account for the effect, for porcelain, which is fired at a far higher temperature than glass, gives off a copious supply of gases consisting largely of carbon dioxide and hydrogen when heated in a vacuum above 1000°C . If the experiment is prolonged, several cubic centimetres of gas may be pumped off.—*October 21.*
